

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 83109584.9

(51) Int. Cl.³: C 08 F 2/50
 G 03 C 1/68

(22) Date of filing: 26.09.83

(30) Priority: 27.09.82 JP 168088/82

(43) Date of publication of application:
 09.05.84 Bulletin 84/19

(84) Designated Contracting States:
 DE FR GB NL

(71) Applicant: MITSUBISHI CHEMICAL INDUSTRIES
 LIMITED
 5-2, Marunouchi 2-chome Chiyoda-ku
 Tokyo 100(JP)

(72) Inventor: Nagasaka, Hideki
 12-3, Tsukimino 3-chome
 Yamato-shi Kanagawa(JP)

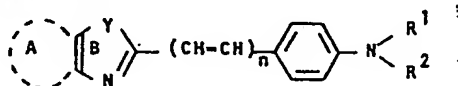
(72) Inventor: Takahashi, Noriaki
 32-7, Fukasawa 4-chome
 Setagaya-ku Tokyo(JP)

(74) Representative: Patentanwälte TER MEER - MÜLLER -
 STEINMEISTER
 Triftstrasse 4
 D-8000 München 22(DE)

(54) Photopolymerizable compositions.

(57) A photopolymerizable composition which comprises an addition-polymerizable compound having at least one ethylenically unsaturated double bond and a photopolymerization initiator system, characterized in that said photopolymerization initiator system essentially consists of

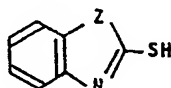
(a) a p-dialkylaminostyrene derivative or p-dialkylaminophenylbutadiene derivative represented by the general formula



wherein R₁ and R₂ independently represent an alkyl group; Y represents a divalent atom or atomic group selected from the group consisting of -O-, -S- and -CH=CH- and forms aromatic heterocyclic ring B together with trivalent nitrogen atom, and ring A represents a benzene ring or naphthalene ring condensed with ring B, and n is 1 or 2;

(b) a hexaaryl-biimidazole; and

(c) a thiol compound represented by the general formula



wherein Z represents a divalent atom or atomic group selected from the group consisting of -O-, -S-, -NH- and



- 2 -

BACKGROUND OF THE INVENTION

1. Field of the Invention:

5 This invention relates to photopolymerizable compositions. More particularly, it relates to photopolymerizable compositions which show high sensitivity to a light source of a visible light range.

2. Description of the Prior Art:

10 A number of image forming methods utilizing photopolymerizable systems are known. For instance, there is known a method of forming an image whereby a

photopolymerizable composition which comprises a compound having an addition-polymerizable ethylenically unsaturated bond and a photopolymerization initiator, and optionally organic polymer binders, thermal polymerization inhibitors, colorants, plasticizers and the like is prepared; this photopolymerizable composition is applied onto a support either in the absence of any solvent or after dissolution in solvents, thereby forming a photosensitive material having a photopolymerizable composition layer thereon; and the photosensitive material is exposed to light in a desired image pattern, so that the exposed portions are polymerized and cured, and the remaining non-exposed portions are dissolved out and removed, thereby forming a cured relief image. Alternatively, a photosensitive material is made by forming a photosensitive layer between two supports at least one of which is transparent; the photosensitive material is exposed in an imagewise pattern from the transparent support side, thereby causing the photosensitive layer to vary in adhesion strength; and thereafter the supports are separated from each other to form the intended image on the support. Still alternatively, there is a method of image formation which utilizes a change in toner adherence of a photopolymerizable composition layer on exposure to light.

The photopolymerization initiators for the photopolymerizable compositions used in the above methods are, for example, benzoine, benzoine alkyl ethers, benzophenone, anthraquinone, benzil, and Michler's ketone.

5 However, these photopolymerization initiators have much lower photopolymerization initiating ability to a light source of the visible light region exceeding 400 nm than to a light source of the ultraviolet region below 400 nm. This places a great limit on the range
10 of application of photopolymerizable composition comprising these initiators.

Several photopolymerization systems which are sensitive to visible light have been heretofore proposed. In the past, it was described in U. S. Patent No. 2,850,445
15 that certain kinds of photo-reducible dyes, e.g. Rose Bengal, Eosine, erythrosine, riboflavin and the like, had an effective visible light sensitivity. Since then, improvements have been reported including composite initiator systems comprising dyes and
20 aliphatic amines (Japanese Patent Publication No. 20189/1969, systems of hexaarylbiimidazoles, radical generators, and dyes (Japanese Patent Publication No. 37377/1970, systems of hexaarylbiimidazoles and (p-dialkylaminobenzylidene) ketones (U. S. Patent Nos.
25 3,652,275 and 4,162,162), systems of cyclic-cis-alpha-dicarbonyl compounds and dyes (U. S. Patent No.

3,756,827), and systems of substituted triazines and merocyanine dye (Japanese Patent Application Laid-open No. 151024/1979). These systems are effective to visible light but are not satisfactory with regard to their photosensitive velocity. Thus, there is a continuing need for further improvements.

Some of the present inventors have already proposed photopolymerizable compositions which are highly sensitive to visible light (Japanese Patent Application Laid-open No. 21401/1982 and Japanese Patent Application Laid-open No. 19315/1983).

SUMMARY OF THE INVENTION

It has now been found that when a specific type of thiol compound is used in combination with a specific type of photopolymerization initiator, a photopolymerizable composition of improved sensitivity can be obtained. This composition can be conveniently applied, for example, to the field of plate making by direct irradiation of a laser beam. This permits the shortened time of making one plate and easy plate-making by a laser beam of low output power. The present invention is accomplished based on the above finding.

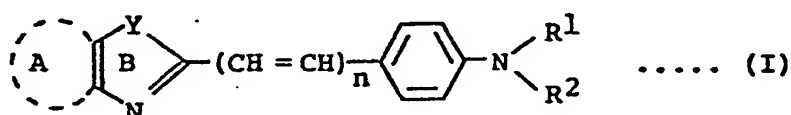
The subject matter of the present invention resides in a

- 5 -

photopolymerizable composition which comprises an addition polymerizable compound having at least one ethylenically unsaturated double bond and a photopolymerization initiator system, characterized in that said photopolymerization

5 initiator system essentially consists of:

- (a) a p-dialkylaminostyrene derivative or p-dialkylaminophenylbutadiene derivative represented by the general formula



10 wherein R^1 and R^2 independently represent an alkyl group; Y represents a divalent atom or atomic group selected from the group consisting of -O-, -S-, and -CH=CH- and forms aromatic heterocyclic ring B together with trivalent nitrogen atom, and ring A

15 represents a benzene ring or naphthalene ring condensed with ring B, and n is 1 or 2;

- (b) a hexaaryl-biimidazole; and
- (c) a thiol compound represented by the general formula



wherein Z represents a divalent atom or atomic group selected from the group consisting of -O-, -S-, -NH- and -CNH-.



DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The addition-polymerizable compound having at least one ethylenically unsaturated double bond which is one of the essential components in the photopolymerizable composition of the present invention is a monomer having an ethylenically unsaturated double bond or a polymer having an

10 ethylenically unsaturated double bond in the side or main chain. The monomer or polymer should be cured and rendered substantially insoluble by addition polymerization by the action of a photodecomposed product from a photopolymerization initiator, which is the second essen-

15 tial component, when the photopolymerizable composition is subjected irradiation of actinic light. The term "monomer" used herein is intended to mean a concept relative to so-called polymer materials and cover, aside from monomers in a strict sense, dimers, trimers, and

20 oligomers.

Examples of the monomers having the ethylenically unsaturated double bond include unsaturated carboxylic acids,

esters of unsaturated carboxylic acids and aliphatic polyhydroxy compounds, esters of unsaturated carboxylic acids and aromatic polyhydroxy compounds, and esters obtained by the esterification reaction of unsaturated
 5 carboxylic acids, polycarboxylic acids, and polyhydroxy compounds such as aliphatic polyhydroxy compounds, aromatic polyhydroxy compounds and the like.

The esters of aliphatic polyhydroxy compounds and unsaturated carboxylic acids are, for example, acrylates such as
 10 ethylene glycol diacrylate, triethylene glycol diacrylate, trimethylolpropane triacrylate, trimethylolethane triacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate,
 15 dipentaerythritol hexaacrylate, glycerol acrylate and the like; methacrylates such as triethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetra-
 20 methacrylate, dipentaerythritol dimethacrylate, dipentaerythritol trimethacrylate, dipentaerythritol tetramethacrylate and the like; itaconates such as ethylene glycol diitaconate, tetramethylene glycol diitaconate, pentaerythritol triitaconate and the like; crotonates such
 25 as ethylene glycol dicrotonate, diethylene glycol

dicrotonate, pentaerythritol tetracrotonate and the like; and maleates such as ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate and the like.

The esters of aromatic polyhydroxy compounds and unsaturated carboxylic acids include hydroquinone diacrylate, hydroquinone dimethacrylate, resorcin diacrylate, resorcin dimethacrylate, pyrogallol triacrylate, and the like.

The esters obtained by the esterification of unsaturated carboxylic acids, polycarboxylic acids, and polyhydroxy compounds are not necessarily single products. Illustrative of such esters are condensates of acrylic acid, phthalic acid and ethylene glycol; condensates of acrylic acid, maleic acid and diethylene glycol; condensates of methacrylic acid, terephthalic acid and pentaerythritol; condensates of acrylic acid, adipic acid, butanediol and glycerol.

Examples of other compounds having an ethylenically unsaturated double bond used in the present invention include acrylamides such as ethylene bisacrylamide, allyl esters such as diallyl phthalate, vinyl group-containing compounds such as divinyl phthalate, and the like.

The polymers having an ethylenically unsaturated bond in the main chain thereof include, for example, polyesters obtained by polycondensation between unsaturated

dicarboxylic acids and dihydroxy compounds; polyamides obtained by polycondensation between unsaturated dicarboxylic acids and diamines, and the like.

5 The polymers having an ethylenically unsaturated bond in the side chain thereof include polycondensation products of dicarboxylic acids having an unsaturated bond at the side chain thereof, e.g. itaconic acid, propylidenesuccinic acid, ethylidenemalonic acid and the like with dihydroxy or diamine compounds. Polymers having a hydroxy group or
10 a halogenated methyl group in the side chain thereof such as, for example, polymers obtained by polymerization reaction between polyvinyl alcohol, poly(2-hydroxyethylmethacrylate), polyepichlorohydrin or the like and unsaturated carboxylic acids such as (metha)acrylic acid,
15 crotonic acid or the like may also be conveniently used.

Of these addition-polymerizable compounds having at least ethylenically unsaturated double bond, the monomers of acrylates or methacrylates are preferably used.

The photopolymerization initiator which is the second
20 essential ingredient of the photopolymerizable composition according to the present invention are described below.

The photopolymerization initiator systems must produce radicals on irradiation of actinic light and bring about the addition polymerization reaction of the compound

having the ethylenically unsaturated bond. The initiator system of the present invention consists of a combination of three ingredients. The first ingredient (a) is a p-dialkylaminostyrene derivative or p-dialkylaminophenyl-

5 butadiene derivative represented by the afore-mentioned general formula (I) wherein R¹ and R² is preferably methyl or ethyl, respectively. Examples of such derivative include p-dialkylaminostyrene derivatives such as 2-(p-

10 dimethylaminostyryl)benzothiazole, 2-(p-diethylaminostyryl) benzothiazole (hereinafter referred to as "a-1"), 2-(p-

dimethylaminostyryl)benzoxazole (hereinafter referred to as "a-2"), 2-(p-diethylaminostyryl)benzoxazole, 2-(p-

dimethylaminostyryl)benzo[4,5]benzothiazole (hereinafter referred to as "a-3"), 2-(p-diethylaminostyryl)benzo[4,5]

15 benzothiazole (hereinafter referred to as "a-4"), 2-(p-diethylaminostyryl)benzo[6,7]benzothiazole, 2-(p-dimethylaminostyryl)quinoline (hereinafter referred to as "a-5"),

2-(p-diethylaminostyryl)quinoline, 2-(p-diethylaminostyryl)benzo[4,5]benzoxazole, and the like; and dialkylamino-

20 phenylbutadiene derivatives such as 2-[4-(p-dimethylamino-phenyl)-1,3-butadienyl]benzothiazole (hereinafter referred to as "a-6"), 2-[4-(p-diethylaminophenyl)-1,3-butadienyl]

benzothiazole, 2-[4-(p-di-n-butylaminophenyl)-1,3-butadienyl]benzothiazole, 2-[4-(p-dimethylaminophenyl)-

25 1,3-butadienyl]benzo[6,7]benzothiazole (hereinafter

referred to as "a-7"), 2-[4-(p-diethylaminophenyl)-1,3-butadienyl]benzo[4,5]benzothiazole (hereinafter referred to as "a-8"), and the like.

These compounds are prepared by condensation reaction
5 between a corresponding p-dialkylaminobenzaldehyde or p-dialkylaminocinnamic aldehyde and a 2-methylheterocyclic compound, for example, according to the method described in Zhur. Obshchei. Khim 26, 2891 - 6 (1956).

The second ingredient (b) is a hexaaryl-biimidazole.
10 This compound is also called 2,4,5-triarylimidazolyl dimer which has such a structure that two imidazoles are combined through one covalent bond.

The aryl groups are preferably phenyl groups. The phenyl group may have a substituent. Especially, hexaphenyl-
15 -biimidazole in which the phenyl groups at 2 and 2' positions on the imidazole ring are substituted at the ortho position with fluorine, chlorine, bromine, nitro or methyl are preferred from the standpoint of thermal stability and photoreaction velocity.

20 Preferred examples of the hexaaryl-biimidazoles include 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-biimidazole (hereinafter referred to as "b-1"), 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenyl-biimidazole

(hereinafter referred to as "b-2"), 2,2'-bis(o,p-dichlorophenyl)-4,4',5,5'-tetraphenyl-biimidazole (hereinafter referred to as "b-3"), 2,2'-bis(o-chlorophenyl-4,4',5,5'-tetra(m-methoxyphenyl)-biimidazole, 2,2'-bis(o,o'-dichlorophenyl)-4,4',5,5'-tetraphenyl-biimidazole (hereinafter referred to as "b-4"), 2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetraphenyl-biimidazole (hereinafter referred to as "b-5"), 2,2'-bis(o-methylphenyl)-4,4',5,5'-tetraphenyl-biimidazole (hereinafter referred to as "b-6"), and the like.

These hexaaryl-biimidazoles are readily prepared according to the methods described, for example, in Bull. Chem. Soc. Japan, 33, 565 (1960) and J. Org. Chem. 36 [16] 2262 (1971).

It has also now been found that the sensitivity could be improved by several times by adding a specific thiol compound in addition to the above two ingredients.

Thiol compounds are known as a typical radical chain transfer agent. References 1.- 3 appearing hereinafter demonstrate effects of the introduction into the conventional, typical photopolymerization initiator systems of the thiol compound on sensitivity. From this, it can be seen that the sensitivity is remarkably improved only when thiol compounds are added to a specific type of

polymerization initiator system.

The thiol compounds as the ingredient (c) of the present invention are those represented by the foregoing general formula (II). Specific examples of the compounds include

5 2-mercaptobenzothiazole (hereinafter referred to as "c-1"),
2-mercaptobenzoxazole (hereinafter referred to as "c-2"),
2-mercaptobenzimidazole (hereinafter referred to as "c-3"),
2-mercapto-4(3H)quinazolinone (hereinafter referred to as
"c-4"), and the like.

10 The amounts of the ingredients (a), (b) and (c) used in the photopolymerizable composition according to the present invention are, respectively, 0.1 - 10 parts by weight, preferably 1 - 7 parts by weight for the ingredient (a), 0.5 - 30 parts by weight, preferably 2 - 15 parts by weight

15 for the ingredient (b), and 0.1 - 20 parts by weight, preferably 1 - 15 parts by weight for the ingredient (c), all based on 100 parts by weight of the ethylenically addition-polymerizable compound.

In addition to the above ingredients, the photopolymeri-

20 zable composition of the present invention may further contain organic polymer materials as a binder in order to modify the composition and improve physical properties after photo-curing. The binder is properly chosen depending on the purpose of the improvement in properties such

as compatibility, film-forming property, developability, and adhesiveness. For instance, the improvement in developability of an aqueous system can be achieved by the use of (metha)acrylic acid copolymers, itaconic acid

5 copolymers, partially esterified maleic acid copolymers, acidic cellulose-modified products having carboxyl groups at the side chain thereof, polyethylene oxide, polyvinylpyrrolidone, and the like. In order to improve the film strength and adhesiveness, a polyether of epichlorohydrin

10 and bisphenol A, soluble nylons, polyalkyl methacrylates such as polymethyl methacrylate, polyalkyl acrylate, copolymers of alkyl methacrylates and acrylonitrile, acrylic acid, methacrylic acid, vinyl chloride, vinylidene chloride, styrene or the like, copolymers of acrylonitrile

15 and vinyl chloride or vinylidene chloride, copolymers of vinylidene chloride, chlorinated polyolefins or vinyl chloride and vinyl acetate, polyvinyl acetate, copolymers of acrylonitrile and styrene, copolymers of acrylonitrile and butadiene or styrene, polyvinyl alkyl ethers, poly-

20 vinyl alkyl ketones, polystyrene, polyamides, polyurethanes, polyethylene terephthalate isophthalate, acetyl cellulose, polyvinyl butyral, and the like. These binders may be added in an amount in the range of not more than 500%, preferably not more than 200% based on the weight

25 of the compound having ethylenic bond.

The photopolymerizable composition of the present invention may further comprise thermal polymerization inhibitors, colorants, plasticizers, surface protecting agents, smoothing agents, application aids, and the like, if necessary.

The thermal polymerization inhibitors include, for example, hydroquinone, p-methoxyphenyl, pyrogallol, catechol, 2,6-di-t-butyl-p-cresol, beta-naphthol, and the like. The colorants include, for example, pigments such as phthalocyanine pigments, azo pigments, carbon black, titanium oxide and the like, and dyes such as Ethyl Violet, Crystal Violet, Azo dyes, anthraquinone dyes, cyanine dyes and the like. These thermal polymerization inhibitors and colorants are conveniently used in amounts of from 0.01 to 3% and from 0.1 to 20%, respectively, both based on the total weight of the ethylenically unsaturated double bond-bearing compound and the binder. The plasticizers include, for example, dioctyl phthalate, didodecyl phthalate, triethylene glycol dicaprylate, dimethyl glycol phthalate, tricresyl phosphate, dioctyl adipate, dibutyl sebacate, triacetyl glycerol, and the like. The plasticizers are added in an amount not more than 5% based on the total weight of the ethylenically unsaturated double bond-bearing compound and the binder.

The photopolymerizable composition of the present invention

may be used to form a photosensitive material in the absence of solvents, or may be dissolved in suitable solvents to give a solution, followed by applying it onto a support and drying to obtain a photosensitive material.

- 5 The solvents are, for example, methyl ethyl ketone, cyclohexanone, butyl acetate, amyl acetate, ethyl propionate, toluene, xylene, monochlorobenzene, carbon tetrachloride, trichloroethylene, trichloroethane, dimethylformamide, methyl cellosolve, ethyl cellosolve, tetrahydrofuran,
10 pentoxone, and the like.

- Supports to which the photopolymerizable composition of the present invention is applied for the formation of a photosensitive material thereon includes, for example, sheets of metals such as aluminium, magnesium, copper,
15 zinc, chromium, nickel, iron and the like, and alloys thereof, paper sheets such as high quality papers, art papers, release papers and the like, sheets of inorganic materials such as glasses and ceramics, sheets of polymers such as polyethylene terephthalate, polyethylene, poly-
20 methyl methacrylate, polyvinyl chloride, vinyl chloride-vinylidene chloride copolymers, polystyrene, 6-nylon, cellulose triacetate, and cellulose acetate butylate, and the like.

- The photopolymerizable composition of the present inven-
25 tion may be treated by known techniques for the prevention

of disadvantageous effects of oxygen, such as lowered sensitivity, deterioration of storage stability and the like. For instance, a photosensitive layer may be covered with a releasable transparent cover sheet, or a
5 coating layer of a wax-like material or a water-soluble polymer which has a small oxygen permeability.

The light sources applicable to the composition of the present invention include general-purpose light sources irradiating ultraviolet and visible light with wavelengths
10 not less than 180 nm, e.g. carbon arc lamps, high pressure mercury lamps, xenone lamps, metal halide lamps, fluorescent lamps, tungsten lamps, argon ion lasers, and the like.

The photopolymerizable composition of the present invention has uses in a wide range of fields and can be used
15 in the preparation of printing plates for use in a lithograph, intaglio and relief printing or the like; photoresists for the preparation of printed circuit or IC and dry films; image formation of relief images and reproduction of images; photocurable inks; paints; adhesives or
20 the like. Especially, they are useful in the field where a light source for visible light is applied.

Having generally described the invention, a more complete understanding can be obtained by reference to certain

specific examples, which are included for purposes of illustration only and are not intended to be limiting unless otherwise specified.

5 The abbreviations for the respective ingredients used in the examples, comparative examples and references correspond to those compounds indicated before. The amounts are expressed by weight percent based on the total weight of an ethylenic monomer and a binder.

Example 1 and Comparative Examples 1 - 3

10 1.0 g of a methyl methacrylate/methacrylic acid copolymer (binder) obtained by 20 mol % partial hydrolysis of polymethyl methacrylate BR-83 (product by Mitsubishi Rayon Co., Ltd.) by a usual manner, 1.0 g of trimethylolpropane triacrylate (product by Osaka Organic Chem. Ind.
15 Co., Ltd.), 6 mg of p-methoxyphenol and 6 mg of Victoria Pure Blue BOH (product by Hodogaya Chemical Co., Ltd.) were dissolved in 18 g of methyl ethyl ketone, thereby obtaining a stock solution for photosensitive solution. This stock solution was admixed with ingredient additives
20 indicated in Table 1, and was applied to an aluminium sheet, which had been sand-blasted and anodized, by the use of a whirler so that a dry thickness was 2 μ m, followed by drying at 80°C for 5 minutes. Thereafter, an aqueous polyvinyl alcohol solution was applied onto the

coating surface so that an overcoat layer with a dry thickness of 3 μm was formed, thereby obtaining a sample. A step tablet (product of Eastman Kodak Co.) was superposed on the sample in a vacuum printing frame, followed by exposing to light. The sample was exposed to light ray (light intensity of 1.0 mW/cm²) with a wavelength of about 490 nm which had been obtained from a xenone lamp after passing through a color glass filter Y-47 and an interference filter KL-49 (both made by Toshiba Glass Co., Ltd.) for 10 seconds. After completion of the exposure, the exposed sample was developed with an aqueous solution containing 9 wt. % of butyl cellosolve and 1 wt. % of sodium silicate. The sensitivity was determined in terms of step number of the resultant photo-cured image. The results are shown in Table 1.

Table 1

	Ingredient (a) [amount]	Ingredient (b) [amount]	Ingredient (c) [amount]	Sensitivity
Example 1	a-4 [2.5%]	b-1 [5%]	c-1 [5%]	7 (step)
Comp. Ex. 1	" "	" "	-	3
20 " 2	" "	-	c-1 [5%]	0
" 3	-	b-1 [5%]	" "	0

The sample of Example 1 was found to have a sensitivity 4 times or more as high as the samples of Comparative Examples 1 through 3.

Examples 2 - 7 and Comparative Examples 4 - 7

- 5 Example 1 was repeated except that 5 wt. % of b-2 was added to and dissolved in the stock solution of Example 1 as the ingredient (b), and compounds indicated in Table 2 were added as the ingredients (a) and (c). The resulting samples were evaluated under the same conditions in
- 10 Example 1.

Table 2

		Ingredient (a) [amount]		Ingredient (c) [amount]		Sensitivity
15	Example 2	a-4	[2.5%]	c-2	[5%]	7 (step)
	" 3	a-8	"	"	"	7
	" 4	a-7	"	"	"	6.5
	" 5	a-3	"	"	"	7
	" 6	a-4	"	c-3	"	6.5
20	" 7	"	"	c-4	[2%]	5.5
	Comp. Ex. 4	a-4	"	-		3
	" 5	a-8	"	-		2.5
	" 6	a-7	"	-		3
	" 7	a-3	"	-		2.5

Examples 8 - 12 and Comparative Examples 8 - 12

Example 1 was repeated except that 5 wt. % of b-2 as the ingredient (b) was added to and dissolved in the stock solution obtained in Example 1, and compounds indicated in Table 3 were added, as the ingredients (a) and (c), to the solution, and that the sample was exposed to a light ray with a wavelength of 436 nm (light intensity of 0.065 mW/cm^2), which had been obtained from a high pressure mercury lamp after passage through a color glass filter L-42 and an interference filter KL-43 (both made by Toshiba Glass Co., Ltd.) for 50 seconds. The results are shown in Table 3.

Table 3

		Ingredient (a) [amount]		Ingredient (c) [amount]		Sensitivity
15	Example 8	a-4	[2.5%]	c-2	[5%]	5.5 (step)
	" 9	a-5	"	"	"	4
	" 10	a-2	"	"	"	5.5
	" 11	a-1	"	"	"	5
	" 12	a-6	"	"	"	5
20	Comp. Ex. 8	a-4	"	-	-	2
	" 9	a-5	"	-	-	0
	" 10	a-2	"	-	-	2
	" 11	a-1	"	-	-	1
	" 12	a-6	"	-	-	1

Examples 13 - 16 and Comparative Examples 13 and 14

Example 1 was repeated except that 2.5 wt. % of a-4 as the ingredient (a), and compounds indicated in Table 4 as the ingredients (b) and (c) were added to the stock

5 solution used in Example 1. The results are shown in Table 4.

Table 4

		Ingredient (b) [amount]	Ingredient (c) [amount]	Sensitivity
10	Example 13	b-3 [5%]	c-1 [5%]	7 (step)
	" 14	b-4 "	" "	4.5
	" 15	b-5 "	" "	5.5
	" 16	b-6 "	" "	5
	Comp. Ex. 13	b-4 "	-	1
	" 14	b-6 "	-	1.5

15 Examples 17 - 20

Example 1 was repeated using, instead of trimethylolpropane triacrylate, ethylenic monomers indicated in Table 5. The results are shown in Table 5.

Table 5

		Ethylenic Monomer	Sensitivity
-	Example 17	pentaerythritol triacrylate	7 (step)
"	18	pentaerythritol tetramethacrylate	7
5	"	1,6-hexanediol diacrylate	6.5
"	20	glycerol monoacrylate	6

Example 21

The sample used in Example 1 was exposed to light by scanning with an argon ion laser. The laser beam having a wavelength of 488 nm was focused on the sample surface at a beam diameter of 15 μ m so that the sample was exposed to light under conditions of a light intensity of 15.7 mW and a scanning speed of 51.3 m/sec. Thereafter, the development as in Example 1 was effected to obtain cured lines having a width of 15 μ m.

References 1 - 3

The stock solution used in Example 1 was admixed with 5 wt. % of each of ordinary photopolymerization initiators and further with 5 wt. % of thiol c-1, thereby comparing their sensitivities with one another. The results are shown in Table 6.

Table 6

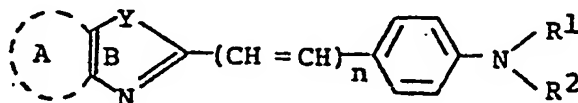
	Photopolymerization Initiator	Effect of c-1
5	Reference 1 benzoin methyl ether	lowering of sensitivity by 0.5 step
	Reference 2 2-ethylanthraquinone	lowering of sensitivity by 6 steps
10	Reference 3 benzil + Michler's ketone	no change in sensitivity

Having now fully described this invention, it will be
apparent to one of ordinary skill in the art that many
changes and modifications can be made thereto without
departing from the spirit or scope of the invention as
15 set forth herein.

WHAT IS CLAIMED AS NEW AND INTENDED TO BE COVERED BY
LETTERS PATENT IS:

1. A photopolymerizable composition which comprises an addition-polymerizable compound having at least one ethylenically unsaturated double bond and a photopolymerization initiator system, characterized in that said photopolymerization initiator system essentially consists of:

(a) a p-dialkylaminostyrene derivative or p-dialkylaminophenylbutadiene derivative represented by the general formula

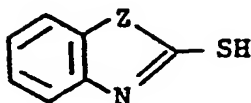


wherein R^1 and R^2 independently represent an alkyl group, Y represents a divalent atom or atomic group selected from the group consisting of -O-, -S- and -CH=CH- and forms aromatic heterocyclic ring B together with trivalent nitrogen atom, and ring A represents a benzene ring or naphthalene ring condensed with ring B, and n is 1 or 2;

(b) a hexaaryl-biimidazole; and

26
- 27 -

- (c) a thiol compound represented by the general formula



wherein Z represents a divalent atom or atomic group selected from the group consisting of -O-,
-S-, -NH- and -CNH-.



2. The composition according to Claim 1, wherein the addition-polymerizable compound having at least one ethylenically unsaturated bond is an acrylate or methacrylate.
3. The composition according to Claim 1, wherein the p-dialkylaminostyrene derivative or p-dialkylaminophenylbutadiene derivative is 2-(p-dialkylaminostyryl)benzo[4,5]benzothiazole, 2-(p-dialkylaminostyryl)benzothiazole or 2-(p-dialkylaminostyryl)benzooxazole.
4. The composition according to Claim 1, wherein the hexaaryl-biimidazole is 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-biimidazole or 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenyl-biimidazole.
5. The composition according to Claim 1, wherein the thiol compound is 2-mercaptobenzothiazole or 2-mercaptobenzoxazole.



European Patent
Office

EUROPEAN SEARCH REPORT

0107792

Application number

EP 83 10 9584

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
D, Y	US-A-3 652 275 (M.D. BAUM et al.) * Claim 1 *	1-5	C 08 F 2/50 G 03 C 1/68
Y	GB-A-2 029 423 (AGFA-GEVAERT N.V.) * Claim 1 *	1-5	
Y	FR-A-2 337 890 (DYNACHEM CORP.)	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 08 F G 03 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18-01-1984	Examiner CAUWENBERG C.L.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.